Enhanced luminescence in Er^{3+}-doped chalcogenide glass-ceramics based on selenium

Mathieu Hubert[a], Laurent Calvez[a,*], Xiang-Hua Zhang[a] and Pierre Lucas[b]

[a] Equipe Verres et Céramiques, UMR 6226 Institut des Sciences Chimiques de Rennes, Campus de Beaulieu, Avenue du Général Leclerc, 35042, Rennes, France

*laurent.calvez@univ-rennes1.fr

Tel: (33) 2 23 23 67 13

Fax: (33) 2 23 23 56 11

[b] Arizona Materials Laboratory, 4715 East Fort Lowell Rd, Tucson, AZ, 85712, USA

pierre@email.arizona.edu

Abstract

Rare earth doped glass-ceramics transparent in the infrared region up to 16 µm have been prepared and studied. The enhancement of the emission of Er^{3+} ions at 1.54 µm with increasing crystallinity was demonstrated in a selenium-based glass-ceramic having a composition of $80GeSe_2$-$20Ga_2Se_3$+1000 ppm Er. The optical transmission, microstructure and luminescence properties of a base glass and glass-ceramics were investigated. Luminescence intensities up to 7 times greater were obtained in glass-ceramics in comparison to the base glass. These materials are promising candidates for the production of new laser sources in the mid-infrared region.

Keywords: Chalcogenide glasses; glass-ceramics; rare-earth; luminescence

1. Introduction

While many commercial laser sources are available in the visible and near IR region, efficient laser sources in the mid-IR are rare or limited to a few wavelengths such as CO_2 laser at 10.6 microns. The low phonon energy of chalcogenide glasses presents two major advantages for the production of laser materials operating in the infrared region. First they generate a transparency window that extends far in the infrared, up to 20µm [1]. Second, low phonons improve the radiative emission quantum efficiency of rare-earth (RE) ions dissolved in the glass matrix. In addition, several studies have reported an enhancement of the luminescence in sulfur-based glass-ceramics in comparison to the base glass due to the presence of a crystalline environment surrounding the rare-earth ions [2, 3]. It has been postulated that the change in crystalline-field during nucleation results in longer radiative lifetimes.

Such crystallization effects have never been reported in selenide glass matrices despite the fact that selenium-based glasses should provide even lower phonon energies and wider infrared transparency, thereby enabling the design of laser sources at longer wavelengths. In addition, like sulfur-based glasses [4, 5], selenium-based chalcogenide glasses have shown reproducible and controllable crystallization behavior conducive to the production of glass-ceramics with enhanced mechanical properties while keeping high infrared transparency up to long wavelengths [6, 7]. Hence, selenide glass matrices are promising candidates for the design of RE doped glass-ceramics. Furthermore, compositions containing gallium are of particular interest as several studies have shown that the addition of gallium in chalcogenide glasses enhances the RE ions dissolving capacity [8, 9]. In that respect, the $80GeSe_2$-$20Ga_2Se_3$ glass composition represents a good potential host for RE ions doped glass-ceramics with enhanced luminescence intensities. In fact, it has shown a controllable and reproducible behavior towards crystallization [6, 10] and it possesses a high content of gallium (11.8 at%).

In the following study, the introduction of erbium in $80GeSe_2$-$20Ga_2Se_3$ glasses will be investigated for the production of RE doped glass-ceramics. Their emissions in the infrared and their lifetimes as a function of the crystallization will be characterized to study the correlation between the crystalline environment and emission efficiency.

2. Experimental procedure

Bulk glasses having a composition of $80GeSe_2$-$20Ga_2Se_3$+ 1000 ppm Er were prepared by melting the highly pure raw Ga (Cerac, 6N), Ge (Umicore, 5N), Se (Umicore, 5N) and metallic Er (Strem Chemicals, 3N) under vacuum (~10^{-3} Pa) in a sealed silica ampoule. The ampoule of 9 mm inner diameter was inserted into a rocking furnace, heated up to 850^{o}C for 12 h, and then quenched into water. The obtained glass was annealed below the glass transition temperature (T_g-10°C) for 3 h to minimize inner constraints, and finally slowly cooled down to room temperature. The glass rod was then cut and polished to produce discs of about 2 mm of thickness. Glass-ceramics were produced by heat treating the disks in a ventilated furnace at 380°C (Tg+10°C) for several hours as described in a previous study [6].

Optical transmission measurements were carried out using a UV/Vis/NIR Perkin Elmer Lambda 1050 spectrometer between 0.6 µm and 2 µm, and a Bruker Vector 22 spectrophotometer in the mid-IR region ranging from 2 µm to 20 µm with an accuracy of ± 2%.

X-Ray diffraction (XRD) data were collected between 10° and 70° (°2θ) on bulk glasses and glass ceramics using a Phillips PW3020 diffractometer (Voltage 40 kV, current 30 mA) with Cu Kα radiation and a step width of 0.02°.

The observation of the glass and glass–ceramics microstructure was realized by using a scanning electronic microscope (FEG-SEM JEOL 7400F). The samples were coated with a gold thin film prior to observation due to the insulating character of the samples. Observation was done in fracture surfaces on the coated sample to prevent any confusion with the coating structure.

The refractive index of the materials was measured on optically polished bulk samples by means of the prism coupling technique (Metricon-2010 instrument). A laser beam at wavelengths k = 1.06 µm, 1.31 µm and 1.54 µm and a rutile prism were used.

Near infrared photoluminescence was measured at room temperature by using a FLSP920 spectrometer (Edinburgh Instruments) equipped with a nitrogen cooled NIR PMT detector and a tunable CW 450W Xenon Arc Lamp as the excitation source. A pulsed xenon lamp (Microsecond Flashlamp µF920H, Edinburgh Instruments) was used as excitation source for lifetime measurements.

3. Results

3.1. Crystallization of the base glass

SEM micrographs (x20,000) of the base glass and of the glass-ceramics are presented in Fig. 1. No crystals are observed in the base glass after quenching (Fig. 1a). This allows to subsequently inducing a homogeneous crystallization by heat treatment above Tg. After 10 h of ceramization, small particles are generated in the glassy matrix (Fig. 1b). These particles are composed of aggregates of about 100 nm of diameter of crystals of smaller dimension, as observed in similar glass-ceramics [6]. The amount of particles generated increases after 20 h (Fig. 1c), 50 h (Fig. 1d) and 80 h (Fig. 1e) of heat treatment at 380°C. It is noteworthy that although their quantity is more important, the size of the aggregates does not increase with increasing duration of heat treatment.

XRD spectra in Fig. 2 show a progressive crystallization of the glass with the duration of heat treatment. While a broad signal characteristic of an amorphous material is observed on the base glass, crystallization peaks appear on the spectra collected on the glass-ceramics. The peaks become sharper with the duration of heat treatment. This confirms an increase of the crystallinity in the glass-ceramics. The peaks become sharper with the duration of heat treatment. This confirms an increase of the crystallinity in the glass-ceramics. The peaks observed are attributed to

the Ga_2Se_3 crystalline phase. From SEM micrographs in Fig. 1, the estimated crystallinity is 10 %, 30 % and 50 % after 10 h, 20 h and 50 h of crystallization, respectively.

3.2. Optical transmission

The optical transmission of the base glass (GCEr0) and glass-ceramics heat treated at 380°C for 10 h (GCEr10), 20 h (GCEr20), 50 h (GCEr50) and 80 h (GCEr80) is presented in Fig. 3. The base glass presents a transmission ranging from 0.7 µm up to 16 µm. Visible and near-infrared transmission from 0.6 µm to 2 µm is shown in the inset in Fig. 3. A progressive shift of the optical band gap towards longer wavelengths with heat treatment duration is observed for the glass-ceramics. This red-shift can be related to the increasing amount of crystals inside the glassy matrix, inducing Rayleigh scattering. However, glass-ceramics transmission in the mid-infrared range remains almost unchanged up to 80 h of heat treatment, demonstrating that no MIE scattering occurs. Both of these observations demonstrate that glass-ceramics are constituted of very small particles.

Absorption bands due to the transitions between the energy levels $^4I_{15/2} \rightarrow {}^4I_{9/2}$, $^4I_{15/2} \rightarrow {}^4I_{11/2}$ and $^4I_{15/2} \rightarrow {}^4I_{13/2}$ of the Er^{3+} ions are observed at 820 nm, 980 nm and 1.54 µm, respectively. The RE ions have been incorporated in the glassy matrix. The absorption bands located around 4.5 µm and 12.5 µm correspond to the vibration of Se-H and Ge-O bonds. A distillation step could allow to get rid of these parasite vibrations.

3.3. Refractive index

The precipitation of crystals within the glassy matrix induces a change in the refractive index (n) of the material. The refractive index values measured on the base glass (GCEr0) and a glass-ceramic after 50 h of heat treatment at 380°C (GCEr50) at three different wavelengths are presented in Table 1. From this table, it appears that the precipitation of the crystalline phase significantly increases the value of *n* by up to 0.03 after 50 h of ceramization.

3.4. Luminescence

The luminescence intensity for the radiative emission corresponding to the transition $^4I_{13/2} \rightarrow {}^4I_{15/2}$ under 823 nm excitation pump is presented in Fig. 4. The inset shows the energy levels of the Er^{3+} ions, located at 0 cm^{-1}, 6450cm^{-1}, 10200 cm^{-1} and 12195 cm^{-1}, for the $^4I_{15/2}$, $^4I_{13/2}$, $^4I_{11/2}$ and $^4I_{9/2}$ levels, respectively. After excitation to the $^4I_{9/2}$ level, a de-excitation leads to the population of the $^4I_{13/2}$ level, which then radiatively decays to the $^4I_{15/2}$ level with an emission at 1.54 µm.

A broad emission centered at 1535 nm with a full width at half maximum (FWHM) of 50 nm is observed in the base glass and in the glass-ceramics. The maximum intensity of luminescence is progressively enhanced with increasing

heat treatment duration. The emission is up to 7 times higher in the sample heat treated for 50 h (GCEr50) in comparison with the base glass (GCEr0). However, the shape of the peak remains similar whatever the duration of heat treatment, indicating that the Er^{3+} ions remain in the glassy phase and are not incorporated inside the crystals [11]. No luminescence is measured for the glass-ceramics heat-treated for 80 h. This absence of emission may be explained by the high crystallinity of the glass-ceramic. An excessive amount of crystals led to a loss of transparency in the 1.54µm region.

3.5. Lifetime measurements

The Er^{3+} $^4I_{13/2}$ energy level lifetime was measured in the base glass and in the glass-ceramics by exciting the $^4I_{9/2}$ level at 823nm. The fluorescence decay curves for the glass and the glass-ceramics presented a similar shape whatever the crystallization time. As a matter of clarity, only one of the decay curves is presented in Fig. 5. A rise time is observed due to the excitation via the decay of the $^4I_{9/2}$ level followed by the decay of the $^4I_{13/2}$ energy level itself. The curves show two decay components, a fast decay component (fdc) with a relaxation rate τ_1 and a slow decay component (dsc) with a relaxation rate τ_2. The lifetimes τ_1 and τ_2 were calculated by fitting the decay curves by a dual exponential expression of the form $I_f(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$. The results are presented in Table 2. A ratio A_1 of 2% of the Er^{3+} ions decay with lifetime τ_1 and a ratio A_2 of 98% with lifetime τ_2, whatever the crystallization time.

4. Discussion

While direct measurements for Er^{3+} ions lifetimes usually show a single exponential component, it is common to observe stretched or multi-exponential components when the measurements are indirect [12]. In the case of this study, the excitation wavelength used is 823 nm and is therefore indirect, explaining the observation of two exponential components (fdc and sdc) on the lifetime measurements. The fast decay component can be explained by an Energy Transfer Upconversion (ETU) process between adjacent Er^{3+} ions. It has been demonstrated for Er:YAG lasers that the depopulation of the $^4I_{13/2}$ energy level can be provoked by ETU between two Er^{3+} ions [2], following a two photons phenomena $(^4I_{13/2}, {}^4I_{13/2}) \rightarrow (^4I_{15/2}, {}^4I_{9/2})$ [13]. Half of the ions are upconverted to the excited level $^4I_{9/2}$ while the other half relaxes to the $^4I_{15/2}$ level. This depopulation process is very fast, with a decay rate on the order of the microsecond [14]. Er^{3+} ions have to be close enough for ETU to occur, which is likely to be due to a partial clustering of the erbium ions, as suggested by Shah et al [12]. The random nature of the clustering does not allow for an interpretation of evolution of the values measured for τ_1.

The spontaneous emission probability of RE ions (A) can be derived from the Judd-Ofelt theory. It is proportional to the emission cross-section of the RE ion $\sigma_e(\upsilon)$ and to the radiative lifetime τ. I can be calculated from the following equation [15]: $A = 1/\tau = (8\pi n^2/c)\int \upsilon^2 \sigma_e(\upsilon) d\upsilon$, where n is the refractive index of the host matrix and c is the velocity of light in vacuum. It thus appears from this equation that an increase of the refractive index n of the host matrix will lead to increased spontaneous emission probabilities and decreased lifetimes. As indicated in Table 1, the refractive index of the host matrix increases significantly with the progressive crystallization within the glass-ceramics. This increase in the values of n therefore leads to an increase of the spontaneous emission probability and thus to the enhancement of the luminescence intensity observed as well as the decrease of the lifetimes τ_2 measured.

The enhanced luminescence observed in the present glass-ceramics is very promising for the development of laser sources in the mid-infrared. Many rare-earths possess potential radiative transitions in the 4-12 µm region which are well within the transmission window of selenide glass-ceramics. These materials could therefore enable the production of novel laser source with high quantum efficiency in a range of wavelength of strategic importance for defense and bio-medical applications.

5. Conclusions

Rare earth doped selenium-based glass-ceramics have been prepared and their luminescence properties have been studied. A base glass having a composition of $80GeSe_2$-$20Ga_2Se_3$ doped with 1000 ppm of Er was prepared and heat treated to produce glass-ceramics transparent in the infrared region. XRD and SEM analyses showed crystallization of a Ga_2Se_3 phase inside the glassy matrix, with an increased crystallinity after longer duration of heat treatment. Absorptions due to the energy levels of the Er^{3+} ions were observed. The emission at 1.54µm was monitored in the base glass and in the glass-ceramics. The emission intensity was up to 7 times higher after 50 h of heat treatment as compared to the base glass. This enhancement of the luminescence intensity was accompanied by a reduction of the radiative lifetimes measured. These observations have been correlated with the increase in the refractive index of the host matrix with crystallinity. This study demonstrates the possibility of preparing RE doped chalcogenide glass-ceramics based on selenium with a good transparency in the infrared up to 16 µm. This work constitutes the first step towards the design of materials interesting for the production of new laser sources in the mid-infrared region.

6. Acknowledgements

This work has been supported by the National Science Foundation (NSF Grant# DMR-0844014) and the AFOSR DURIP Grant FA9550-10-1-0282.

7. References

1. P. Lucas, M.R. Riley, C. Boussard-Plédel, B. Bureau, Anal. Biochem. 351 [1] (2006) 1-10
2. R. Balda, S. Garcia-Revilla, J. Fernández, V. Seznec, V. Nazabal, X.H. Zhang, J.L. Adam, M. Allix, G. Matzen, Opt. Mater. 31 [5] (2009) 760-764
3. V. Seznec, H.L. Ma, X.H. Zhang, V. Nazabal, J.L. Adam, X.S. Qiao, X.P. Fan, Proc. SPIE - Int. Soc. Opt. Eng. 6116 [3] (2006) B1-9
4. H.L. Ma, L. Calvez, B. Bureau, M. Le Floch, X.H. Zhang, J. Lucas, J. Phys. Chem. Sol. 68 [5-6] (2007) 968-971
5. Y. Ledemi, B. Bureau, L. Calvez, M. Le Floch, M. Rozé, C. Lin, X.H. Zhang, M. Allix, G. Matzen, Y. Messaddeq, J. Phys. Chem. B 113 [44] (2009) 14574-14580
6. M. Rozé, L. Calvez, Y. Ledemi, M. Allix, G. Matzen, X.H. Zhang, J. Am. Ceram. Soc. 91 [11] (2008) 3566-3570
7. L. Calvez, H.L. Ma, J. Lucas, X.H. Zhang, Adv. Mater. 19 [1] (2007) 129-132
8. A. Zakery, S.R. Elliott, J. Non-Cryst. Sol. 330 [1-3] (2003) 1-12
9. D.T. Tonchev, C.J. Haugen, R.G. DeCorby, J.N. McMullin, S.O. Kasap, J. Non-Cryst. Sol. 326-327 (2003) 364-368
10. M. Rozé, L. Calvez, M. Hubert, P. Toupin, B. Bureau, C. Boussard-Plédel, X.H. Zhang, Int. J. Appl. Glass Sci. 2 [2] (2011) 129-136
11. E. Guillevic, M. Allix, X.H. Zhang, J.L. Adam, G. Matzen, X.P. Fan, Mat. Res. Bull. 45 [4] (2009) 448-455
12. M. Shah, M. Wojdak, A.J. Kenyon, M.P. Halsall, H. Li, I.F. Crowe, J. Lumin. 132 [12] (2012) 3103-3112
13. C. Raulin, S. Karsai, Laser and Ipl Technology in Dermatology and Aesthetic Medicine, 1st ed. Springer, New York, 2011.

14. C.C. Ye, P.R. Morkel, E.R. Taylor, D.N. Payne, Proc. 19th Europ. Conf. Opt. Commun (ECOC) (1993) 73-76

15. M. Li, Y. Lin, H. Hu, Proc. SPIE, Rare-Earth-Doped Materials and Devices IV 3942 (2000) 261-266

Figure caption list

Fig. 1: SEM micrographs (x20,000) of the $80GeSe_2$-$20Ga_2Se_3$+1000 ppm Er after a) 0 h; b) 10 h; c) 20 h; and d) 50 h of heat treatment at 380°C

Fig. 2: Evolution of the XRD diffraction patterns for different heat treatment durations for the $80GeSe_2$-$20Ga_2Se_3$+1000 ppm Er glass composition

Fig. 3: Optical transmission of the $80GeSe_2$-$20Ga_2Se_3$+1000 ppm Er base glass and glass-ceramics

Fig. 4: Emission of the $80GeSe_2$-$20Ga_2Se_3$+1000 ppm Er glass and glass-ceramics pumped at 823nm. The inset shows the energy diagram for the Er^{3+} ions

Fig. 5: Decay curve measured on Er-doped $80GeSe_2$-$20Ga_2Se_3$ base glass and glass-ceramics

Table 1: Refractive index *n* of the base glass (GCEr0) and a glass-ceramic heat treated for 50 h at 380°C (GCEr50) measured at three different wavelengths

Table 2: Lifetimes calculated for the Er-doped $80GeSe_2$-$20Ga_2Se_3$ glass-ceramics as a function of ceramization time